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(54) Title: METHOD FOR SANITIZING SWIMMING POOLS AND RECIRCULATING WATER SYSTEMS

(57) Abstract

A method of treating the water of a swimming pool equipped with a skimmer basket by placing bromochlorodimethylhydantoin in the skimmer basket and a cationic polymer in the pool.

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METHOD FOR SANITIZING SWIMMING POOLS
AND RECIRCULATING WATER SYSTEMS

FIELD OF THE INVENTION

5 The present invention relates generally to methods for sanitizing recirculating water systems, and more particularly to a method of using N-halogenated hydantoins to sanitize swimming pools.

BACKGROUND OF THE INVENTION

10 N-halogenated hydantoins such as bromochlorodimethyl-hydantoin have long been recognized as effective disinfectants for circulating water systems. For example, in 1964 Paterson disclosed the use of bromochlorodimethylhydantoins as disinfectants for swimming pool water after recognizing that organo-bromo-chlorinated
15 compounds appeared to have enhanced bacteriacidal activity when compared to disinfecting compositions containing bromine or chlorine alone. See, U.S. Patent No. 3,147,219.

Unfortunately, it has also long been recognized that there are significant problems associated with effectively
20 delivering N-halogenated hydantoins to swimming pool water. Paterson initially studied and "solved" the problem with respect to bromochlorodimethylhydantoin in U.S. Patent No. 3,412,021, issued in 1968, by suggesting that bromochlorodimethyl- hydantoins should be delivered as a
25 solid agglomerate disposed in a reservoir "so that the surface area of the agglomerates exposed to the impure water is held substantially constant." See, U.S. Patent No. 3,412,021 at col. 3. lines 44-51.

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In recognition of the accepted view that N-halogenated hydantoins such as bromochlorodimethylhydantoins should be delivered by placing an agglomerate of the disinfectant in a reservoir constructed so that a constant surface area of the agglomerate is exposed to the water, the prior art developed the use of separate "brominator" chemical dispensing devices to dispense the N-halogenated hydantoin product. Examples of such "brominators" include the Di-Halo® Automatic Swimming Pool Disinfecting System and the Aquabrome® Brominator.

Certain disadvantages are known to be associated with brominator dispensing systems. For example, swimming pools in geographical areas prone to freezing temperatures must winterize all plumbing equipment, including the brominator chemical dispensing device. This is a time consuming process, and may subject the pool owner and/or operator to unnecessary chemical exposure when purging the brominator of agglomerated or tableted hydantoin. In addition, the consumption rate of dimethylhydantoin is greater than necessary when brominator units are used.

A need therefore exists for a method of disinfecting swimming pools with N-halogenated hydantoins such as dihalodimethylhydantoins, whereby disinfectant consumption is reduced, the need for associated plumbing and equipment is eliminated, and superior water quality is maintained. The present invention addresses that need.

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SUMMARY OF THE INVENTION

Briefly describing one preferred embodiment of the present invention, there is provided a method of treating the water of a swimming pool by putting an agglomerate of bromochlorodimethylhydantoin in the skimmer basket, and a cationic polymer in the pool, and allowing a substantial portion of the agglomerate to dissolve before replenishing the supply of agglomerate in the skimmer basket.

One object of the present invention is to provide an improved method of delivering N-halogenated hydantoin to swimming pool water.

Another object of the present invention is to provide an improved method of delivering BCDMH to swimming pool water.

Further objects and advantages of the present invention will be apparent from the following description.

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DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the invention as illustrated therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

One preferred embodiment of the present invention relates to an improved method of effectively providing bromochloro-5,5- dimethylhydantoin ("BCDMH" or bromochloro-5,5-dimethyl-2,4- imidazolidinedione) to swimming pool water. In the prior art, a special "brominator" dispensing apparatus was understood to be required to provide a bed of BCDMH agglomerate that contacts the pool water as it is pumped through the pool filter. In another preferred embodiment other N-halogenated hydantoins are used.

The present invention eliminates the requirement to have a separate chemical dispensing device for delivering dihalodimethylhydantoins to the pool. Instead, one preferred embodiment of the present invention effectively delivers bromochlorodimethylhydantoin to swimming pool water by placing one or more pucks of BCDMH in the pool's skimmer basket and replacing the pucks only after they have substantially dissolved. With this method the surface area of the BCDMH is not constant as it would be with prior art methods.

In another preferred embodiment, bromochlorodimethylhydantoin is effectively delivered by placing pucks of BCDMH in the skimmer basket in conjunction with the addition of a

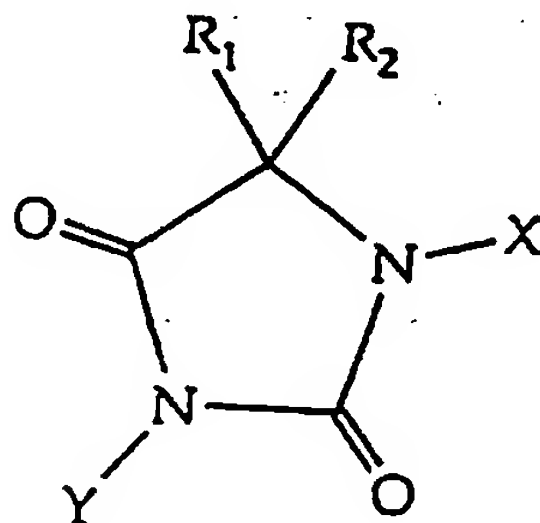
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cationic polymer to the pool water. Here too, the surface area of the BCDMH is not constant as it would be with prior art methods.

5 In a third preferred embodiment, an N-halogenated composition is added to a recirculating water system by contacting the recirculating water with solid pieces of the N-halogenated composition, wherein the surface area of the N-halogenated composition is allowed to vary over time (i.e., the surface area is not kept substantially
10 constant). In this embodiment the N-halogenated composition need not be placed in the skimmer basket, but may be maintained in contact with the recirculating water at any convenient location by placing the N-halogenated composition in a receptacle which allows the recirculating water to
15 freely flow therethrough.

In one aspect of the present invention a method is provided for reducing the consumption of N-halogenated hydantoins when the same are used to treat recirculating water. For example, the use of prior art brominator
20 chemical dispensing devices is difficult to regulate and results in an average consumption of 3 to 5 pounds of bromochlorodimethylhydantoin per week per 10,000 gallons. In contrast, the skimmer-fed application of tableted bromochlorodimethylhydantoin accompanied by the biweekly
25 addition of cationic polymeric compounds results in an average BCDMH consumption rate of only 1 to 2 pounds per week per 10,000 gallons.

As to the compositions themselves, the N-halogenated hydantoin is preferably of the formula:



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where:

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a lower
(C₁₋₈) alkyl, a lower (C₁₋₈) acyl, or a lower (C₁₋₈)
5 alkoxy; and

R₁ and R₂ are each C₁₋₈ mono- or multivalent
hydrocarbon radicals of the group consisting of alkyl and/or
saturated or unsaturated monocyclic hydrocarbon radicals
having five or six carbon atoms per cycle, which radicals
10 can be substituted with lower alkyl, lower acyl, lower
alkoxy, carboxy and/or sulfonic acid groups.

As previously indicated, bromochlorodimethylhydantoin is
preferably used. Other N-halogenated hydantoins with higher
order straight or branched chain alkyl groups in Position 5
15 of the heterocyclic imidazolidinedione ring may be more or
less desired according to the particular characteristics
desired to be achieved, and according to other technical and
economic considerations.

The N-halogenated hydantoin may be provided in either
20 dry or liquid form. When provided as a dry composition, the
hydantoin may be agglomerated, compressed, extruded or
tableted into essentially any size or shape. Preferably,
the N-halogenated hydantoin is formed into tablets weighing
from 1 to 500 grams. More preferably, the N-halogenated
25 hydantoin is provided as an agglomerated, compressed,
extruded or tableted product of undefined dimension, size
and/or shape weighing from 10 to 200 grams. Most
preferably, the N-halogenated hydantoin is provided as an
agglomerated, compressed, extruded or tableted product of
30 undefined dimension, size and/or shape weighing from 20 to
125 grams. The N-halogenated hydantoin used in certain of
the following examples was provided as a 1" diameter, 20
gram compressed tablet or a 2 3/4" diameter, 120 gram
compressed puck.

35 In one preferred embodiment of the present invention,

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one or more pucks of bromochlorodimethylhydantoin agglomerate are placed directly in the skimmer basket of a pool. The pucks are allowed to dissolve in the pool water over a period of between about three days and about seven days before new pucks are added to the skimmer basket to replenish the supply. In this embodiment of the invention the agglomerate is provided in an amount and in a form such that the surface area of the agglomerate exposed to the water changes over time as the pucks dissolve, and is not substantially constant.

In another preferred embodiment the N-halogenated hydantoin is delivered to the recirculating water via a device which holds the hydantoin and is placed in the recirculating water flow. For example, the N-halogenated hydantoin may be placed in a reusable or a disposable container which holds the hydantoin while simultaneously allowing water to flow freely therethrough. The container is preferably corrosion resistant, and may be an interlocking clam shell device, or a twist-open or permeable mesh bag-type assembly. The receptacle may be maintained in contact with the water at essentially any location in the pool or its associated plumbing. Most preferably, the receptacle is placed in the skimmer basket.

The total halogen is preferably between 0.1 and 10.0, expressed as mg/liter Br_2 . More preferably, total halogen is between 0.25 and 2.5 mg/liter Br_2 . In one preferred embodiment the total halogen is between 0.40 to 0.80 mg/liter Br_2 .

In one preferred embodiment of the present invention, a secondary composition is provided to the pool water to work in conjunction with the bromochlorodimethylhydantoin. In the most preferred of these embodiments the bromochlorodimethylhydantoin agglomerate is delivered through the skimmer basket technique previously described, and the secondary composition is added directly to the

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pool. The secondary composition is preferably added to the pool at least once a month, more preferably every ten to twenty days, and most preferably biweekly.

The secondary composition preferably exhibits properties such as water clarification, halogen residual stabilization, etc., in circulating water systems. Preferably the secondary composition is a polymer; most preferably a cationic polymer. Polymeric and/or non-polymeric substances that are rigid, water soluble clarifying agents in any physical form such as aluminum sulfate, ferric salts, iron III compounds, etc., may advantageously be used.

In certain preferred embodiments the secondary composition is a water soluble cationic polymer such as poly(hexamethylammonium chloride), poly(dodecamethylene-dimethylimino chloride), poly[(oxyethylene dimethylimino)ethylene-(dimethylimino)ethylene dichloride], 1,3-diaza-2,4-cyclopentadiene (with 1-chloro-2,3-epoxypropane to assist in water clarification and filtration), polyvinyl amine, chitosan, polyethylene amine or a polymer of 1,6-hexanediamine-N,N,N',N'-tetramethyl. Alternatively, the fluoride, chloride, or bromide salts of these compounds may also be used.

The molecular weight of the cationic polymer is preferably between about 500 Da to 100,000 Da, with polymers having a molecular weight of between about 1,000 Da and 20,000 Da being most preferred.

The cationic polymer is preferably provided at a concentration of about 0.10 to 10.0 mg/liter as active cationic. More preferably, the polymeric cationics should be present in a concentration of about 0.75 to 7.5 mg/liter as active cationic. Most preferably, the polymeric cationics should be present in a concentration of about 1.0 to 4.0 mg/liter as active cationic.

Reference will now be made to specific examples using

the processes described above. It is to be understood that the examples are provided to more completely describe preferred embodiments, and that no limitation to the scope of the invention is intended thereby.

5

Examples 1 through 4

The field performance of prior art methods of delivering bromochloro-5,5-dimethylhydantoin was evaluated. The compound was delivered by placing 20 gram, 1" diameter tablets in a "brominator" chemical dispensing device.

10

The following information was recorded during each pool visit. (1) Date and time of pool inspection; (2) pH; (3) total alkalinity as mg/l CaCO_3 ; (4) calcium hardness as mg/l CaCO_3 ; (5) observed total bromine residual as ppm bromine; (6) water temperature ($^{\circ}\text{F}$); (7) total dissolved solids; (8) copper and iron content; (9) cyanuric acid (Stabilizer) content as mg/l cyanuric acid; (10) turbidity as NTU's; (11) pounds of N-halogenated compound added; (12) Brominator Chemical Dispensing Device setting; and (13) general pool appearance (visual).

15

20

The test period was June-September, with most pools being tested weekly over a 12-15 week period.

EXAMPLE 1

25

The system represented in Example 1 is a 14,770 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filtering system and a pump. The pool was equipped with an AQUABROME® Brominator Chemical Dispensing device CR8.19AT plumbed in a pressure-suction configuration. The pool operated approximately 12 hours per day.

30

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.7 pounds

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per week per 10,000 gallons. The average observed turbidity ranged between 0.05 and 0.49, with an average observed turbidity of 0.17 for the trial period. The average observed total residual bromine was 1.48 ppm. No algae formation was observed during the test period.

EXAMPLE 2

The system represented in Example 2 is a 21,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a high rate sand filter and a pump. The pool was originally treated with stabilized chlorine (e.g., trichloro-s-triazinetriene) via skimmer feed, but was fitted with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction configuration. The pool operated approximately 12 to 14 hours per day.

During the trial period the average consumption rate of tableted Bromochloro-5,5-dimethylhydantoin was 5.0 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.06 and 0.47, with an average observed turbidity of 0.19 for the trial period. The average observed total residual bromine was 1.59 ppm. No algae formation was observed during the test period.

EXAMPLE 3

The system represented in Example 3 is a 21,500 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a high rate sand filter and a pump. The pool was equipped with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction configuration. The pool operated routinely from 12 to 24 hours.

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.43 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.43, with an average observed

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turbidity of 0.20 for the trial period. The average observed total residual bromine was 1.46 ppm. No algae formation was observed during the test period.

EXAMPLE 4

5 The system represented in Example 4 is a 15,400 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a cartridge filter system and a pump. The pool was fitted with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction
10 configuration. The pool operated routinely from 12 to 24 hours per day.

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.35 pounds per week per 10,000 gallons.

15 It can be seen from the above that the methods of the prior art provide bromochlorodimethylhydantoin to swimming pool water at an average consumption rate of about 4.2 pounds per week per 10,000 gallons for outdoor residential swimming pools of between about 10,000 and about 25,000
20 gallons. The average observed turbidity ranged between 0.09 and 0.49, with an average observed turbidity of 0.26 for the trial period. The average observed total residual bromine was 4.01 ppm. No algae formation was observed during the test period.

25 Examples 5 through 14

Test pools were treated with compressed pucks containing bromochloro-5,5-dimethylhydantoin agglomerate as the active ingredient via skimmer-fed application, and by the direct
30 biweekly addition of 200 ml of a cationic polymeric compound (specifically, poly[hexamethylammonium] chloride) per 10,000 gal. of pool water. The consumption of bromochlorodimethylhydantoin was reduced without sacrificing water quality.

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EXAMPLE 5

5 The system represented in Example 5 is a 29,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and a pump. The pool operated routinely for 12 hours per day, and was facilitated by a timer.

10 During the trial period the average consumption of BCDMH was 1.39 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.58, with an average observed turbidity of 0.23 for the trial period. The average observed total residual bromine was 0.57 ppm. No algae formation was observed during the test period.

EXAMPLE 6

15 The system represented in Example 6 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filter, and a pump. The pool operated approximately 12 hours per day and was not equipped with a timer.

20 During the trial period the average consumption of BCDMH was 0.98 pound per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.60, with an average observed turbidity of 0.24 for the trial period. The average observed total residual bromine was 0.60 ppm. No algae formation was observed during the test period.

EXAMPLE 7

25 The system represented in Example 7 is a 10,000 gallon, outdoor pool. This pool is a vinyl-lined, above-ground system equipped with a makeshift sand filter, and a 1.5 horsepower pump. The pool operated approximately 18 hours per day and was not equipped with a timer.

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During the 14-week trial period the average consumption of BCDMH was 0.72 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.14 and 0.55, with an average observed turbidity of 0.30 for the trial period. The average observed total residual bromine was 0.31 ppm. No algae formation was observed during the test period.

EXAMPLE 8

The system represented in Example 8 is a 27,000 gallon, outdoor pool. This pool is a plaster in-ground system equipped with a cartridge filter and a 1.5 horsepower pump. The pool operated approximately 24 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.45 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.31, with an average observed turbidity of 0.16 for the trial period. The average observed total residual bromine was 1.49 ppm. No algae formation was observed during the test period.

EXAMPLE 9

The system represented in Example 9 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a 1.5 horsepower pump. The pool operated approximately 12 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.10 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.08 and 0.51, with an average observed turbidity of 0.32 for the trial period. The average observed total residual bromine was 0.63 ppm. No algae formation was observed during the test period.

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EXAMPLE 10

The system represented in Example 10 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a 0.75 horsepower pump. The pool operated approximately 24 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 1.93 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.09 and 0.56, with an average observed turbidity of 0.29 for the trial period. The average observed total residual bromine was 1.17 ppm. No algae formation was observed during the test period.

EXAMPLE 11

The system represented in Example 11 is a 32,500 gallon, outdoor pool. This pool is a plaster, in-ground system equipped with a D.E. filter, and a 1.0 horsepower pump. The filtration system operated approximately 10 hours per day and was equipped with a timer.

During the 14-week trial period the average consumption of BCDMH was 1.05 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.11 and 0.37, with an average observed turbidity of 0.17 for the trial period. The average observed total residual bromine was 0.59 ppm. No algae formation was observed during the test period.

EXAMPLE 12

The system represented in Example 12 is a 15,100 gallon outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filter and a pump. The pool operated

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approximately 24 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 1.02 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.14 and 0.60, with an average observed turbidity of 0.25 for the trial period. The average observed total residual bromine was 0.71 ppm. No algae formation was observed during the test period.

EXAMPLE 13

The system represented in Example 13 is a 27,000 gallon, outdoor pool. This pool is a plaster, in-ground system equipped with a D.E. filter and a pump. The pool operated approximately 10 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 1.69 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.07 and 0.18, with an average observed turbidity of 0.11 for the trial period. The average observed total residual bromine was 1.38 ppm. No algae formation was observed during the test period.

EXAMPLE 14

The system represented in Example 14 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a pump. The pool operated approximately 24 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.08 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.06 and 0.61, with an average observed turbidity of 0.33 for the trial period. The average observed total residual bromine was 0.77 ppm.

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No algae formation was observed during the test period.

It can be seen from the above that the present invention provides for more finely tuned product delivery rate facilitating a more efficient use of N-halogenated compound than can be obtained by prior art delivery methods. For example, Examples 1 through 4 show that the tested outdoor pool systems using a Brominator Chemical Dispensing Device as directed in Paterson Patent No. 3,412,021 had an average consumption of about 4.6 pounds of tableted

Bromochloro-5,5-dimethylhydantoin per week per 10,000 gallons. In contrast, examples 5-14 show that the tested outdoor pool systems using the skimmer-fed application of tableted Bromochloro-5,5-dimethylhydantoin and the biweekly addition of cationic polymeric compounds resulted in average consumption rate of about 1.2 pounds per week per 10,000 gallons. This is a significant advantage that was not taught or suggested by the prior art.

It can also be seen that water quality was maintained with the inventive skimmer-feed method. In particular, Examples 1 through 4 show that the tested outdoor pool systems using a Brominator Chemical Dispensing Device had an average observed turbidity of 0.21, while examples 5-14 show that the tested outdoor pool systems using the skimmer-fed application of tableted bromochlorodimethylhydantoin and the biweekly addition of cationic polymeric compounds resulted in average observed turbidity of 0.24.

Finally, it can be seen that the skimmer-fed systems of the present invention effectively inhibited algae growth, even when operating at lower-than-conventional total bromine residuals. In particular, effective algae inhibition was observed at residual bromine levels of less than 1.5 ppm, and more particularly at residual bromine levels of less than 1.0 ppm, including at residual bromine levels as low as about 0.3 ppm. The prior art does not teach or suggest

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that effective algael inhibition can be obtained at these low residual bromine levels when bromochlorodimethylhydantoins are used.

EXAMPLE 15

5 The Table below shows bactericidal performance when bromochloro-5,5-dimethylhydantoin is applied at lower residual bromine concentrations. The average bromine residual for examples 6-14 is 0.73 mg/liter. These extremely low bacterial counts provide further support to
10 the proposition that lower residuals of bromochloro-5,5-Dimethylhydantoin are effective in controlling the propagation of bacterial and microbiological contaminants.

TABLE

15 Microbiological Results (CFU's)

| | Example No. | 10 ⁰ | 10 ⁻¹ | 10 ⁻² | 10 ⁻³ |
|----|-------------|-----------------|------------------|------------------|------------------|
| | 6 | CNR | CNR | 0 | 11 |
| | 7 | 0 | 0 | 0 | 0 |
| 20 | 8 | CNR | CNR | CNR | 0 |
| | 9 | 0 | 0 | 0 | 0 |
| | 10 | 0 | 0 | 0 | 0 |
| | 11 | 0 | 0 | 0 | 0 |
| | 12 | 0 | 0 | 0 | 0 |
| 25 | 13 | 0 | 0 | 0 | 0 |
| | 14 | 0 | 0 | 0 | 0 |
| | 15 | 0 | 0 | 0 | 0 |

CNR - Cannot Read

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Examples 16-19 represent test pools that were treated with compressed pucks containing bromochloro-5,5-dimethylhydantoin agglomerate as the active ingredient via skimmer-fed application, without the additional use of a cationic polymer. The consumption of bromochlorohydantoin was reduced without sacrificing water quality.

EXAMPLE 16

The system represented in Example 16 is an 18,400 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.09 pounds per week per 10,000 gallons. The average observed turbidity was between 0.06 and 0.21, with an average observed turbidity of 0.10 for the trial period. The average observed total residual bromine was 0.39 ppm. The average observed cationic polymer concentration was 0.40 ppm. No algae formation was observed during this period.

EXAMPLE 17

The system represented in Example 17 is an 18,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.70 pounds per week per 10,000 gallons. The average observed turbidity was between 0.06 and 0.25,

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with an average observed turbidity of 0.10 for the trial period. The average observed total residual bromine was 0.92 ppm. The average observed cationic polymer concentration was 0.48 ppm. No algae formation was observed during this period.

EXAMPLE 18

The system represented in Example 18 is a 22,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.35 pounds per week per 10,000 gallons. The average observed turbidity was between 0.05 and 0.18, with an average observed turbidity of 0.11 for the trial period. The average observed total residual bromine was 1.25 ppm. The average observed cationic polymer concentration was 0.40 ppm. No algae formation was observed during this period.

20

EXAMPLE 19

The system represented in Example 19 is a 16,000 gallon, outdoor pool. The pool is vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.28 pounds per week per 10,000 gallons. The average observed turbidity was between 0.45 and 0.11, with an average observed turbidity of 0.20 for the trial period. The average observed total residual bromine was 0.85 ppm. The average observed cationic polymer concentration

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was 0.42 ppm. No algae formation was observed during this period.

5 In view of the above it can be seen that with the methods of the present invention substantially lower residuals of bromine concentration may be used to effectively sanitize swimming pool water when bromochlorodimethylhydantoin is applied via the skimmer-fed application described herein.

10 While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and
15 modifications that come within the spirit of the invention are desired to be protected.

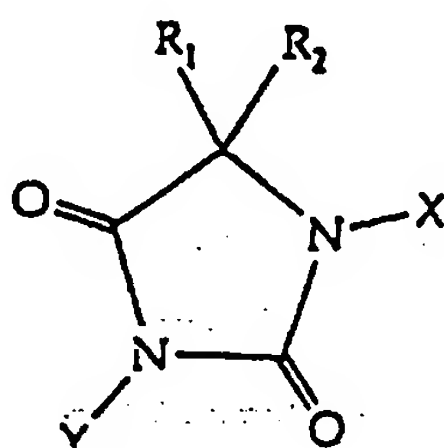
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CLAIMS

What is claimed is:

1. A method of treating the water of a swimming pool equipped with a skimmer basket, comprising the steps of:
 - (a) putting into the skimmer basket an

5 N-halogenated hydantoin of the formula:



where:

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a C₁₋₈ alkyl, a C₁₋₈ acyl, or a C₁₋₈ alkoxy; and

- 10 R₁ and R₂ are each independently a C₁₋₈ monovalent or multivalent hydrocarbon radical selected from the group consisting of alkyl hydrocarbon radicals and saturated or unsaturated monocyclic hydrocarbon radicals having five or six carbon atoms per cycle; wherein said radicals are
- 15 optionally substituted with one or more substituents selected from the group consisting of C₁₋₈ alkyl, C₁₋₈ acyl, C₁₋₈ alkoxy, carboxy and sulfonic acid groups; and
- (b) allowing a substantial portion of the
- 20 N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the skimmer basket.

2. The method of claim 1 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.

3. The method of claim 1 wherein said N-halogenated

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compound is provided as an agglomerate, and wherein said "allowing" step comprises allowing a substantial portion of the agglomerate to dissolve before replenishing the supply of agglomerate in the skimmer basket.

5 4. The method of claim 1 wherein said N-halogenated compound is provided to the skimmer basket by placing the N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.

10 5. In a method of treating the water of a swimming pool equipped with a skimmer basket, wherein the swimming pool water is treated with both an N-halogenated compound and an additional water clarifying composition, the improvement comprising providing the N-halogenated compound
15 to the pool water by placing the N-halogenated compound in the skimmer basket and allowing a substantial portion of the N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the skimmer basket.

20 6. The method of claim 5 wherein said additional water clarifying composition is a cationic polymer.

 7. The method of claim 5 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.

 8. The method of claim 6 wherein said cationic polymer is added to the water biweekly.

25 9. The method of claim 5 wherein said N-halogenated compound is provided to the skimmer basket by placing the N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.

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10. A method of treating the water of a swimming pool equipped with a skimmer basket, said method comprising the step of providing an N-halogenated compound to the skimmer basket of a swimming pool in an amount and form effective to
5 provide between about 0.2 and 1.0 ppm of the N-halogenated compound to the water.

11. The method of claim 10 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.

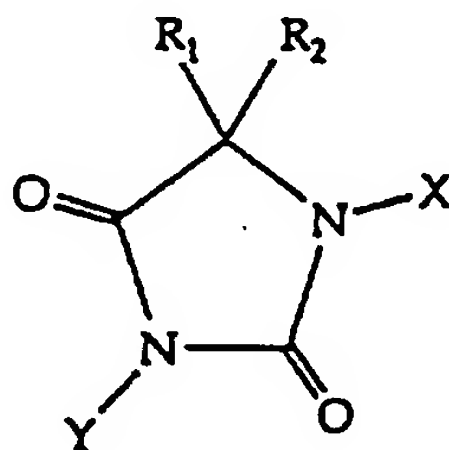
12. The method of claim 10, and additionally including
10 the step of providing a secondary composition to the pool water to work in conjunction with the N-halogenated composition; wherein said secondary composition is provided to the pool water by placing the secondary composition directly in the pool water.

13. The method of claim 12, wherein said secondary
15 composition is a cationic polymer.

14. The method of claim 10 wherein said N-halogenated compound is provided to the skimmer basket by placing the
20 N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.

15. A method of treating a recirculating water system, said method comprising the steps of:

(a) contacting the recirculating water with an
25 N-halogenated hydantoin of the formula:



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where:

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a C₁₋₈ alkyl, a C₁₋₈ acyl, or a C₁₋₈ alkoxy; and

5 R₁ and R₂ are each independently a C₁₋₈ monovalent or multivalent hydrocarbon radical selected from the group consisting of alkyl hydrocarbon radicals and saturated or unsaturated monocyclic hydrocarbon radicals having five or six carbon atoms per cycle; wherein said radicals are
10 optionally substituted with one or more substituents selected from the group consisting of C₁₋₈ alkyl, C₁₋₈ acyl, C₁₋₈ alkoxy, carboxy and sulfonic acid groups; and
15 (b) allowing a substantial portion of the N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the recirculating water.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/08712

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO2F 1/50

US CL : 210/712

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/712, 721, 725, 728, 732, 734, 735, 736, 755, 764, 765; 162/161; 504/156, 158

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---------------|--|---|
| X --- Y | US 3,412,021 A (PATERSON ET AL) 19 NOVEMBER 1968, SEE ENTIRE DOCUMENT | 1-3, 5, 7, 10, 11, 15 ----- 1-3, 5, 7, 10- 12, 15 |
| Y | US 4,530,120 A (ETANI) 23 JULY 1985, SEE ENTIRE DOCUMENT | 4, 6, 8, 9, 12- 14 |



Further documents are listed in the continuation of Box C.



See patent family annex.

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|---|-----|--|
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Date of the actual completion of the international search

28 JULY 1997

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